Figure 6. Fractograms of a 66.5 SAN/23.5 Solprene 411/10 copo PB–PMMA blend (curve A) and of ABS Cycolac GSM (curve B). Charpy impact tests on notched specimens DIN 53453.

ticles and the matrix is a very important parameter to impart high-impact performances to toughened resins and also that such an adhesion can be provided by using a suitable polymeric emulsifier.

These scanning electron micrographs also demonstrate that the emulsified SAN/SBS blends mainly deform by shear; this response is even more pronounced in our blends than in the commercial ABS. Fractograms confirm that situation; Figure 6 shows indeed that fracture of our blends (A) is much more ductile than that of commercial ABS (B): a definitely higher energy for fracture propagation is indeed recorded for the former, and that possibility to modify the *profile* of the impact response is particularly appealing.

Finally, it is interesting to note that such high-level performances are not detrimental to the Young's modulus of the materials. Values listed in Table II demonstrate that the modulus of our blends is generally higher than that of the commercial ABS and in fact rather close to pure rigid SAN.

When the behavior of PS–PMMA and PB–PMMA copolymers is compared, it can be concluded that a PB block solubilizes more easily in the PB domains of the SBS rubber phase than can a PS block into the corresponding PS domains. That situation was expected considering that, in SBS, PS forms discrete domains in a PB matrix, which therefore is more accessible to the PB blocks of the emulsifier. The effect of the molecular characteristics of these emulsifiers should of course be investigated more deeply.

Nevertheless, the present results, although not fully optimized, demonstrate unambiguously that very high-impact performances can be obtained by simple melt blending a SAN resin with a suitable rubber and an emulsifier such as PB–PMMA copolymer. More systematic experiments are in progress in order to evaluate more precisely the behavior of these materials with respect to the characteristics of the two block copolymers (rubber phase and emulsifier) and composition.

With respect to the technological significance of these results, it is clear that performances of our blends should be optimized as injection-molding materials like the commercially produced ABS are designed. Particular attention should therefore be paid to flow properties, since the present material exhibits a melt viscosity too high for an injection process. Furthermore, optimized commercial ABS resins exhibit a two-phase structure well stabilized against delamination under high shear. It is assumed that our blends behave similarly thanks to the strong interfacial adhesion that has been evidenced.[9] Nevertheless, morphology and impact properties of injection-molded mate-

rials should be evaluated in order to define their real performance level in comparison with classical ABS. Generally speaking, however, the powerfulness of this "blends molecular engineering" concept is once more illustrated and calls for an optimistic approach of still more refined materials optimizations.

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(9) It has been shown indeed to be the case for stabilized polystyrene–polyethylene blends subjected to injection molding.[8]

Model Copolymerization Reactions. Evidence against Participation of a Donor–Acceptor Complex in Reactions of the 1-Butyl Radical with *N*-Phenylmaleimide and 2-Chloroethyl Vinyl Ether

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The participation of electron donor–acceptor (EDA) complexes in alternating radical copolymerizations has been debated for nearly 40 years.[1] It has been suggested that some alternating copolymerizations may not be copolymerizations at all but instead may proceed via successive concerted additions of 1:1 comonomer complexes (**2**) to growing polymeric radicals (**1**)

This is an intriguing idea and, if correct, would explain not only the alternating copolymer structure but also certain kinetic features of alternating copolymerization.[2]

Table I
Consumption of NPM by Addition of 1-Butyl Radical

reactn	[BuHgBr]$_0$[a]	[NPM]$_0$[d]	[CEVE]$_0$	[NPM]$_f$[e]	[7]$_f$	$\dfrac{[7]_f}{[NPM]_0 - [NPM]_f}$
1[b]	0.244	0.268	0.278	0.211	0.0547	96 ± 4%[f]
2[c]	0.226	0.248	0.278	0.147	0.106	105 ± 5
3	0.228	0.245	0.307	0.113	0.111	84 ± 10
4	0.165	0.162	0.211	0.002	0.155	97 ± 4
5	0.159	0.151	0.195	0.001	0.145	97 ± 10
6	0.154	0.154	0.182	0.001	0.161	105 ± 2
7	0.156	0.166	0.204	0.001	0.153	93 ± 4

[a] All concentrations are given in moles per liter. [b] Includes injections after 30 min and 3 h. [c] Includes injections after 30 min and 48 h. [d] Initial [NPM]. [e] Final [NPM]. [f] Reported as mean plus or minus one standard deviation for 2-4 determinations.

But do alkyl radicals undergo such concerted additions? Radical trapping experiments may be used to test this idea and to determine the extent to which complex addition competes with simple addition of uncomplexed olefins (eq 2).

$$
\begin{array}{ccc}
R \cdot \xrightarrow{A} RA \cdot & \xrightarrow{T} & RAT \\
 & & \mathbf{3} \\
\xrightarrow{D} RD \cdot & \xrightarrow{T} & RDT \\
 & & \mathbf{4} \\
\xrightarrow{AD} RAD \cdot & \xrightarrow{T} & RADT \qquad (2) \\
 & & \mathbf{5} \\
\xrightarrow{DA} RDA \cdot & \xrightarrow{T} & RDAT \\
 & & \mathbf{6}
\end{array}
$$
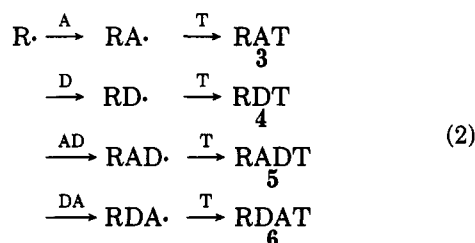
(Here A indicates donor monomer, D indicates acceptor monomer, $\overline{AD}$ indicates complex, and T indicates radical trap.) The radical of interest is generated in the presence of the donor (D) and acceptor (A) monomers, and the resulting adducts are trapped to yield products 3-6. Accurate mass balances for A and D then allow determination of the dominant pathway(s) for monomer consumption.

We have recently reported the use of the "mercury method"[3] in an investigation of the magnitude of penultimate effects in a model styrene-acrylonitrile copolymerization.[4] The needed radicals were generated by hydride reduction of alkyl mercuric halides, and the olefin adducts were trapped by efficient hydrogen atom transfer. The technique is well suited to an investigation of concerted complex addition as outlined in eq 2.

We report in this paper the use of the mercury method to examine the addition of the 1-butyl radical to N-phenylmaleimide (NPM) and 2-chloroethyl vinyl ether (CEVE). Olson and Butler reported recently a very careful analysis of the radical copolymerization of NPM and CEVE and suggest that concerted complex addition dominates the chain-growth process.[5-7] This then appears to be an attractive system in which to demonstrate the use of radical trapping techniques in a test of the complex addition hypothesis.

Experimental Section

Preparations. 1-Butylmercuric Bromide (BuHgBr). 1-Butylmercuric bromide was prepared according to the procedure of Slotta and Jacobi.[8]

2-Butyl-N-phenylsuccinimide. To a solution of 0.44 g (2.54 mmol) of NPM and 0.57 g (1.69 mmol) of 1-butylmercuric bromide in 5 mL of CH_2Cl_2 was added a solution of 0.128 g (3.38 mmol) of $NaBH_4$ in 0.5 mL of H_2O. When no further evolution of gas was apparent, the mixture was analyzed by gas chromatography (9 ft stainless steel column packed with 3% SE-30 on 80/100 Supelcoport; column temp, 180 °C; He flow, 50 mL/min) to monitor the disappearance of 1-butylmercuric bromide. In two subsequent additions, 0.06 and 0.04 mL of a 6.65 M solution of $NaBH_4$ in H_2O were added to the reaction mixture. After the second addition, no BuHgBr was detected. The solution was then

filtered over $MgSO_4$ to remove water. Kugelrohr distillation followed by preparative thin-layer chromatography (3:1 CH_2Cl_2:petroleum ether) yielded 30 mg (10%) of 2-butyl-N-phenylsuccinimide, mp 59 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.9 (triplet, 3 H), 1.2-2.0 (broad, 10 H), 2.6 (multiplet, 1 H), 2.9 (multiplet, 1 H). m/e = 231. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.7; H, 7.4; N, 6.1. Found: C, 72.2; H, 7.3; N, 5.8.

Monomer Mass Balance Experiments. In a typical reaction 0.0445 g (0.257 mmol) of NPM and 0.0368 g (0.300 mmol) of CEVE were added to 0.078 g (0.231 mmol) of BuHgBr in 0.85 mL of CH_2Cl_2. To this solution at room temperature was added 4.54 mg (0.12 mmol) of $NaBH_4$ in 0.1 mL of H_2O. After 30 min, elemental Hg was separated, and the reaction mixture was analyzed by gas chromatography and gas chromatography/mass spectrometry (GC/MS) (9 ft stainless steel column, 3% SE-30 on 80/100 Supelcoport; column temp, 100 °C for 10 min, programmed to 250 °C; He, 50 mL/min). In some experiments, *tert*-butylbenzene was added as an internal chromatographic standard.

Results and Discussion

Generation of the 1-butyl radical by hydride reduction of 1-butylmercuric bromide in solutions of NPM and CEVE provides predominantly 2-butyl-N-phenylsuccinimide (7). Table I summarizes the results of seven trap-

7
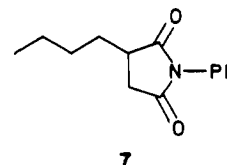
ping experiments and compares the yields of **7** with the amounts of NPM consumed. Although there is some fluctuation in the yields of **7**, on average 97 ± 7% of the reacted NPM appears in this product, regardless of the NPM conversion. Within experimental error, NPM is consumed quantitatively by simple radical addition; concerted complex addition is negligible. Furthermore, we are unable to detect by GC/MS the formation of any compounds of m/e 338, which might have been formed by concerted addition of NPM and CEVE.

These results deserve comment in light of the recent work of Olson and Butler on radical copolymerization of NPM and CEVE.[5-7] On the basis of variations in copolymer ^{13}C NMR spectra with changes in reaction conditions, Olson and Butler suggest that the dominant propagation step in this copolymerization is a concerted addition of a CEVE-terminated macroradical to a 1:1 NPM:CEVE complex. We have repeated the most critical copolymerization experiments of Olson and Butler, and we find them to be readily reproducible. The results in Table I, however, appear inconsistent with the notion that concerted complex addition is the dominant pathway for consumption of NPM in its copolymerization with CEVE.

Might the results in Table I be misleading with regard to the mechanism of the radical copolymerization of NPM

and CEVE? The authors are aware of three possible criticisms: (i) 1-butyl is an imperfect model of a CEVE-terminated macroradical, (ii) the water added in the trapping experiment might affect the postulated NPM: CEVE complex, and (iii) 1-butylmercuric bromide may disrupt the complex. The first criticism is of course a valid one; neither the steric nor the electronic properties of the 1-butyl radical would be expected to duplicate those of a CEVE-terminated macroradical. Our objective in this work is rather more general, however; we wish to determine whether or not concerted complex addition is at all characteristic of alkyl radicals, and so we have selected a very simple model for these initial experiments. A range of radical structures will be examined in the course of this work. In assessing the second criticism, we examined ^{13}C NMR spectra of NPM/CEVE copolymers prepared in CH_2Cl_2 solutions to which H_2O had been added at a concentration equal to that used in the trapping experiments. The spectra were essentially identical with those of samples prepared under dry conditions and varied with feed composition in the manner reported by Olson and Butler.[5,7] Thus the presence of an aqueous phase does not appear to constitute an important difference between our work and theirs. In order to address the third criticism, we examined 300-MHz ^{1}H NMR spectra of CD_2Cl_2 solutions of NPM to which a large excess (31 equiv) of BuHgBr was added. The addition of the organomercurial produced no change in the spectrum of NPM, suggesting no significant change in the electronic properties of the double bond. We would not then expect disruption of the putative NPM: CEVE complex by BuHgBr.[9]

Finally, we have sought evidence in addition to that provided by Olson for the existence of the postulated EDA complex. Addition of up to 84 equiv of CEVE to NPM in CD_2Cl_2 produces no observable change in the 300-MHz ^{1}H NMR spectrum of NPM. Thus we are unable to provide additional support for the existence of the postulated EDA complex. Similar experiments have been used to identify and characterize other 1:1 complexes of electron-

rich and electron-poor olefins.[1]

Conclusions

Trapping experiments show that consumption of NPM by the 1-butyl radical generated in NPM/CEVE solutions occurs essentially only by simple addition of the olefin. No evidence for concerted addition of a comonomer EDA complex is provided.

Registry No. NPM, 941-69-5; CEVE, 110-75-8; BuHgBr, 17774-02-6; 2-butyl-*N*-phenylsuccinimide, 102651-46-7; 1-butyl radical, 2492-36-6.

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